ON

ETHYLENE-PROTOCATECHUIC ACID.

INAUGURAL-DISSERTATION

FOR THE ATTAINMENT OF THE

DEGREE OF DOCTOR OF NATURAL SCIENCE

AT THE

UNIVERSITY OF TÜBINGEN,

UNDER THE PRESIDENCY OF

DR. RUDOLPH FITTIG,

PROFESSOR OF CHEMISTRY,

PRESENTED

BY

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OF PAISLEY, SCOTLAND.

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TO

JAMES BARLOW, ESQUIRE,

OF ACCRINGTON,

A VALUED FRIEND,

THESE PAGES ARE DEDICATED

BY THE

AUTHOR.

In presenting the results of the following investigations to a highly distinguish Faculty, I avail myself of this opportunity to express my warmest thanks to Professor Fittig—who suggested their undertaking and conducted their execution—for the kindness and courtesy he showed me during the period I spent under his teaching.

BEFORE entering on the account of my investigations, it will be necessary to give a review of the labours of those who have been engaged in the study of certain compounds, which bear a close relation to that on which I have been occupied.

Fittig and Mielck*, while engaged on an investigation on the constitution of piperic acid, discovered two new substances which they designated piperonal and piperonylic acid. The first of these, piperonal ($C_8H_6O_3$), was prepared by oxidising piperic acid by hypermanganate of potassium, and was found to be an aldehyde. The second, piperonylic acid ($C_8H_6O_4$), was prepared by the further oxidation of the aldehyde by hypermanganate of potassium. At the same time they proved that neither piperic acid nor piperonal contained hydroxyle, or an alcohol radical held in combination by means of oxygen. In drawing their conclusions as to the constitution of the aldehyde they considered it probable that the two oxygen atoms, besides the one contained in the aldehyde group, were united in the

* Amalen der Chemie u. Pharm., clii, 25.

same way as the two oxygen atoms in quinone. They therefore proposed as the formula for piperonal :

$$C_6H \begin{cases} O''_2 \\ CH_2 \\ CHO \end{cases} \quad \text{or} \quad C_6H_3 \begin{cases} O_2'' \\ CH_2.CHO. \end{cases}$$

These formulæ were merely conditional, and it remained still to study the products of reduction of piperonal and piperonylic acid, to decide positively whether or not they were correct in principle,

In order to solve this question, Fittig and Remsen* undertook an investigation, which had for its first object to decide in what manner the two oxygen atoms were held in combination in piperonal Before shewing what conclusions they drew from tne results of their researches, it will be expedient to shew what these researches were :

"*Action of Barium Hydrate, dilute Hydrochloric Acid, and Water on Piperonylic Acid.*—Ebullition of piperonylic acid with excess of baryta-water for a fortnight gave no decomposition ; from the well known decomposition of the 'ketone acids' by this means, with formation of ketones, the absence of an intervening carbon group whose affinities are partly saturated with oxygen may be probably inferred.

"When it is heated with dilute hydrochloric acid in a sealed tube at 100°, no reaction ensues, but at 170° the clear aud nearly colourless liquid becomes filled with a black substance consisting of unattacked acid and *pure carbon;* no gas whatever is evolved ; the aqueous

* Annalen der Chemie u. Pharm., clix, 129.

solution filtered from the black deposit was found (by evaporation, extraction with ether, precipitation as lead salt, &c.) to contain, as sole product, *protocatechuic acid.* The reaction, therefore, is:

$$\underset{\text{Piperonylic acid.}}{C_8H_6O_4} = C + \underset{\text{Protocatechuic acid.}}{C_7H_6O_4}.$$

"The entire absence of CO and CO_2 in the products of the reaction testifies to the unusual force with which the other two oxygen atoms are combined.

"With pure water, at 170°, piperonylic acid undergoes no change, but at 210° the same production of carbon takes place; a considerable quantity of CO_2 is also evolved, arising from the secondary decomposition of the protocatechuic acid into *pyrocatechin* and CO_2; by recrystallisation from toluene, pyrocatechin was obtained in a perfectly pure state (it is noticeable that by recrystallisation from this menstruum, a much cleaner and purer product is obtained than by any other means heretofore described): pyrocatechin from the above reaction as well as from other sources, thus purified, melted at 102°, whereas other observers have given a higher melting point (111° to 112°); from the perfect identity between the body thus obtained from piperonylic acid and pure pyrocatechin, an analysis was considered superfluous.

"*Action of Phosphoric Chloride on Piperonal.*—When these two bodies in molecular proportions are brought in contact. action ensues in the cold, the mixture becoming hot and fluid; phosphorus oxychloride is formed, together

with an oily substance distilling between 230° and 240°; this does not solidify on standing, cannot be distilled without decomposition, and is decomposed on standing in contact with water. Although this substance was not obtained pure, it was doubtless *piperonal chloride*, $C_8H_6O_2Cl_2$; benzol chloride, $C_6H_5.CHCl_2$, and anisol chloride according to Henry, show analogous properties.

"When one molecule of piperonal and three of phosphoric chloride, act on one another, the same reaction ensues; but on warming again after the complétion of this first stage, a new reaction sets in, gaseous hydrogen chloride being evolved; phosphorus chloride and phosphorus oxychloride distil over on heating, leaving behind an oily liquid boiling with decomposition at about 280°. When this liquid is placed in a damp atmosphere, a cloud of hydrogen chloride is formed and crystals are produced on the side of the vessel: in cold water no action takes place at first, but in a short time decomposition ensues, hydrogen chloride being evolved, and a mass of crystals formed; these cannot be recrystallised from alcohol or from water, as on warming, carbonic and hydrochloric acids are produced; but on dissolving them in alcohol, and adding water till turbidity is produced, long shining colourless needles are obtained; from toluene also this substance can be procured in crystals. The substance thus obtained in crytals from alcohol or from toluene, and the original crystalline mass, alike melted at 90°. The portion purified by treatment with alcohol and water, and dried in vacuo over sulphuric acid, yielded numbers intermediate between those required for the formulæ $C_8H_4Cl_2O_3$ and $C_8H_4Cl_2O_3 + H_2O$; probably, therefore, the compound produced is *hydrate of dichloropiperonal*,

analogous to chloralhydrate, part of the water being lost on drying in vacuo, the reactions being :

$$\underset{\text{Piperonal.}}{C_7H_5O_2.CHO} + PCl_5 = \underset{\text{Piperonal chloride.}}{C_7H_5O_2.CHCl_2} + POCl_3.$$

$$\underset{\text{Piperonal chloride.}}{C_7H_5O_2.CHCl_2} + 2PCl_5 = \underset{\text{Dichloropiperonal chloride.}}{C_7H_3Cl_2O_2.CHCl_2} + 2PCl_3 + 2HCl.$$

$$\underset{\text{Dichloropiperonal chloride.}}{C_7H_3Cl_2O_2.CHCl_2} + H_2O = \underset{\text{Dichloropiperonal.}}{C_7H_3Cl_2O_2.COH} + 2HCl,$$

the last formed substance then uniting with water to form a hydrate. Hence phosphoric chloride does not act on the oxygen-atoms contained in piperonal otherwise than on the aldehyde group CHO.

"*Action of Hot Water on Dichloropiperonal.*—As above stated, this reaction gives rise to the production of CO_2 and HCl; a body crystallisable from water, alcohol, and ether, and containing no chlorine, is simultaneously produced; to get this in the pure state, it is advantageous to exclude air during the action of the water, and to employ toluene as a medium for recrystallisation. On analysis, this body gives numbers agreeing with the formula $C_7H_6O_3$ formed by the reaction $C_8H_4Cl_2O_3 + 2H_2O = C_7H_6O_3 + CO_2 + 2HCl$; it melts at 150°, and is decomposed at a temperature very little higher; its aqueous solution gives an intense and pure green colour with a drop of ferric chloride solution; further addition of a trace of soda-solution gives at first a violet, and on adding more soda, a beautiful red

colouration. The aqueous solution has a weak acid reaction, but ether takes up the substance from a solution supersaturated with sodium carbonate. Its production from an aldehyde renders it probable that the group CHO is retained: in fact it reduces ammoniacal silver solutions; and although no crystalline compound with alkaline bisulphites has been obtained, yet probably such a compound exists, as ether fails to dissolve the substance from a solution shaken with sodio-hydric sulphite. From its properties, mode of formation, and connection with protocatechuic acid, it is without doubt *the aldehyde of this acid.* The production of this acid could not indeed be verified by oxidation, either with nitric acid, permanganate, or chromate and sulphuric acid; but by fusion with potassium hydrate, this oxidising reaction ensues perfectly, and without formation of secondary products, hydrogen being evolved. The acid obtained by this process melted after purification at 199°, and gave numbers agreeing with the formula $C_7H_6O_4 + H_2O$; it also gave the qualitative iron reactions (both with the free acid and its barium salt) for protocatechuic acid.

"*Action of Phosphoric Chloride on Piperonylic Acid.*—This action should give rise to the following series of products:

(1) $C_8H_6O_4 + PCl_5 = C_8H_5O_3.Cl + POCl_3 + HCl.$
(2) $C_8H_5O_3Cl + 2PCl_5 = C_8H_3Cl_2O_3Cl + 2PCl_3 + 2HCl.$
(3) $C_8H_3Cl_2O_3Cl + H_2O = C_8H_4Cl_2O_4 + HCl.$
(4) $C_8H_4Cl_2O_4 + 2H_2O = C_7H_6O_4 + 2HCl + CO_2.$

whereby successively there are produced—(1) *Piperonylic*

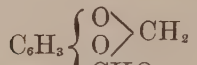
chloride, (2) *Dichloropiperonyl chloride*, (3) *Dichloropiperonylic acid*, and (4) *Protocatechuic acid*.

"On heating one molecule of piperonylic acid with three of phosphoric chloride, there are produced HCl, PCl_3, and $POCl_3$, as required by equations 1 and 2, and a nearly colourless non-solidifying oil of high boiling point, which soon decomposes with cold water, giving hydrochloric acid and an acid containing chlorine, as per equation 3; lastly, this acid heated with water, gives a vigorous effervescence of carbonic anhydride, and forms a solution containing hydrochloric and protocatechuic acids, without a trace of bye-products, the protocatechuic acid thus obtained being chemically pure, as by equation 4. It was not found possible to isolate any of the intermediate products in a state pure enough for analysis; by the action of cold water, as above mentioned, a chlorinated acid was formed; this was evidently a mixture, as it gave the reactions of protocatechuic acid: the percentage of chlorine agrees with that required for an acid which would have the constitution of dichloropiperonylic acid where one Cl-atom was replaced by hydroxyle, or $C_8H_5ClO_5$. The carbon found, however, is upwards of 4 per cent. in excess of that required by this formula.

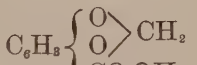
"*Conclusions.*—In the first part of these researches, the view was promulgated that piperonal contains two oxygen-atoms connected together in a manner analogous to that of those in quinone, *i.e.*, that its formula is:

$$C_6H_3\begin{cases} O_2'' \\ CH_2.CHO' \end{cases} \quad \text{or} \quad C_6H_2\begin{cases} O_2'' \\ CH_2 \\ CHO. \end{cases}$$

"The results just obtained completely contradict this view: out of the numerous other constitutional formulæ that might be ascribed, only one fulfils the conditions required by these reactions, viz.:

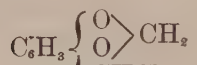


Piperonal.



Piperonylic acid.

where piperonal is the methylene-ether of protocatechuic aldehyde. This view explains the action of nascent hydrogen on the aldehyde and acid, as in the first only the group CHO can be affected, and in the second no action at all can ensue. Baryta-water does not affect phenol-ethers, and would have no action on this acid; under pressure at high temperatures the attraction of the two oxygen-atoms connected with the benzol residue for the hydrogen of the methylene group, would become so powerful as to break up that group, forming hydroxyle and eliminating carbon: hence the action of water and dilute hydrochloric acid. Lastly, Henry has shown* that phosphoric chloride cannot eliminate oxygen which is simultaneously united with two carbon groups.



Piperonal chloride.

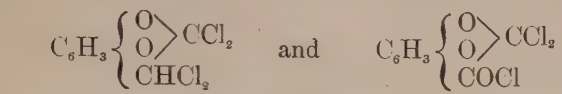
and

Piperonyl chloride.

which are the first products of the action of PCl_5, can lose

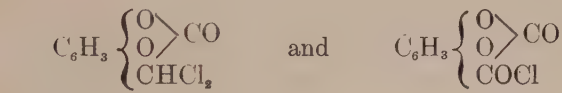
* Deut. chem. Ges. Ber., ii, 710; iii, 704. Ann. Chem. Pharm., clvi, 174.

no more oxygen by the action of this reagent; any further action can only replace hydrogen by chlorine, yielding:



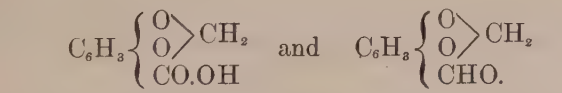
Dichloropiperonal chloride. Dichloropiperonyl chloride

which must be exceptionally unstable, the chlorine last put in being analogous to that of carbonyle chloride $COCl_2$. These compounds in presence of water, must exchange their Cl_2 for O, and the bodies:



thus produced must split up in presence of water, with formation of protocatechuic aldehyde and acid respectively."

As a continuation of the above investigations, the same authors* endeavoured to prove the correctness of their views, that the structural formulæ of these two substances are:



the two bodies being respectively methylene-protocatechuic acid and aldehyde. In order to prove this by synthesis, 1 molecule of pure protocatechuic acid, 3 of caustic potash, and $1\frac{1}{2}$ molecule of methylene iodide were sealed up together and heated for several hours, at first in the water bath, and

* Zeitschrift für Chemie [2], vii, 289.

finally to 140° in an air bath; the nearly black contents of the tube were treated with alcohol; and the extract thus obtained was heated with potassium hydrate for some time to decompose any methylene-ether of methylene-protocatechuic acid; finally hydrochloric acid was added, and the filtrate from the brown amorphous precipitate produced was evaporated. Crystals were thus obtained, which, after recrystallisation, treatment with animal charcoal, and sublimation, possessed all the characters of piperonylic acid, melted at the same temperature, 227°, and were in every respect indistinguishable from that acid.

Just as piperonylic acid, when heated with dilute hydrochloric acid, splits up into carbon and protocatechuic acid, so piperonal when heated to 200° with very dilute acid (10 or 12 volumes water to 1 of concentrated acid), splits up, forming protocatechuic aldehyde and carbon, thus:

$$C_6H_3\begin{cases} O \\ O \\ CHO \end{cases}\!\!\rangle CH_2 \quad = \quad C_6H_3\begin{cases} OH \\ OH \\ CHO. \end{cases}\!\!\rangle + C \text{ "}$$

The reason why I undertook the following series of investigations was to compare the reactions of the two acids, methylene-protocatechuic acid (piperonylic acid) and ethylene-protocatechuic acid.

Wherein these reactions agree or differ, will be seen by a comparison of the results of the investigations.

I.

Ethylene-protocatechuic Acid.

3·5 gramms protocatechuic acid were put into a strong glass tube, and 10 gramms ethylene-bromide poured over it. 4·5 gramms caustic potash were added and the tube hermetically sealed. The tube and its contents were dipped into warm water, kept there for some time, taken out and well shaken, again dipped into the water, and so on until the contents of the tube had changed to a thick brown semi-liquid mass. The tube was then heated for five or six hours in the water bath with occasional shaking to mix the contents. Towards the conclusion of the heating, crystals of bromide of potassium separated out at the bottom of the tube, but the rest of the contents remained as a thick dark liquid. On taking the tube from the bath and allowing it to cool, the whole of the contents became solid; and on opening it there was but little pressure of gas from the inside. The mass was extracted with hot alcohol, the solution slightly warmed, caustic potash added to destroy any ethylene-ether which might be formed, and the alcohol distilled off. The remainder was diluted with water, weak hydrochloric acid added, and the solution shaken with ether. After distilling off the ether, the ethylene-protocatechuic acid remained.

behind as a dark brown mass. By dissolving in water, boiling with animal charcoal, and allowing to crystallise, pure crystals of ethylene-protocatechuic acid were obtained.

In preparing ethylene-protocatechuic acid in this manner it was found very difficult to dissolve the caustic potash and it was therefore found advisable to introduce a slight alteration in the process. After adding the protocatechuic acid, ethylene-bromide and caustic potash in the before mentioned proportions, about a dozen drops of water were added before sealing the tube. (It is advisable not to have more than four gramms of protocatechuic acid in each tube, as so much gas is generated as greatly to endanger the tube.) On heating the tube in warm water the contents darkened at once, and in a very short time became liquid. The tube was then heated for about six hours in the water bath which was kept at the boiling point. On allowing the tube to cool, very few crystals of bromide of potassium appeared, and the contents of the tube remained semi-liquid. On opening the tube there was a strong rush of gas. The contents were dissolved in water, poured into a flask, and the tube rinsed out several times with water. The ethylene-bromide was distilled off with the vapours of water, and the solution acidified with hydrochloric acid.

Whether prepared in this manner or according to that first mentioned, on acidifying with hydrochloric acid a black pitchy substance fell out. It was perfectly insoluble in cold, but slowly dissolved in boiling water. It dissolved in cold water on the addition of a few drops of ammonia, or of a solution of carbonate of soda, from which solution it can be again precipitated by hydrochloric acid. It was slightly soluble in ether

As it possessed such disagreeable properties, and as it proved to be but a secondary product it was thrown away.

The ethylene-protocatechuic acid was extracted by means of ether, and the ether distilled off. The residue was dissolved in water, boiled with animal charcoal, and set aside to crystallise. Two or three crystallisations gave perfectly pure ethylene-protocatechuic acid. A better way however, is to convert it into the lime salt, boil with animal charcoal—heated just before using—filter and crystallise. On filtering off the crystals of the lime salt, washing with a little cold water to get rid of protocatechuate of lime, which is more easily soluble than ethylene-protocatechuate of lime, dissolving in boiling water and acidifying with hydrochloric acid, perfectly pure ethylene-protocatechuic acid was obtained.

In the pure state ethylene-protocatechuic acid crystallises out of water in colourless, indistinct crystals free from water of crystallisation, and out of alcohol in fine clumps of short, glittering prisms. It resembles very much piperonylic acid. It is, like that substance, difficultly soluble in cold water, but in boiling water it dissolves somewhat more readily. In alcohol it is soluble in every proportion. Its melting point is 133·5°.

By cautious sublimation through bibulous paper, between two watch glasses, it was obtained perfectly pure, but when heated above the temperature at which it sublimed, it decomposed and became black. It is preferable not to sublime it except in very small quantities, as it chokes up the paper and gives it a greasy appearance.

The substance was dried by heating to 100° in an air bath. The results of the analysis are as follow :

COMBUSTION.

0·2420 gramm substance gave 0·5318 gramm CO_2=0·145036 C, and 0·1007 gramm H_2O=0·01118 H.

C = 59·93 per cent. H = 4·61 per cent.

These results agree with the formula $C_9H_8O_4$,

	Calculated.		Found.
C_9	108	60·00	59·93
H_8	8	4·44	4·61
O_4	64	35·56	——
	180	100·00	

II.

Diethyl- and Dimethyl-protocatechuic Acids.

Malin* in a notice on these two acids stated that it was his intention to institute a research upon them, but his intentions were frustrated owing to his death which occurred soon after.

It was intended in connection with the research on ethylene-protocatechuic acid to endeavour to prepare Diethyl- and Dimethyl-protocatechuic acids, but before beginning the investigation a paper was published by Koelle† giving the results of his investigations upon the same subject.

* Annalen der Chemie u. Pharmacie clii, 111.

† Deut. chem. Ges. Ber., iv, 634.

"*Dimethyl-protocatechuic acid* is prepared by heating 1 gramm of protocatechuic acid, 4 gramms of methyl iodide, and 1 gramm of pure potash, together with some methyl alcohol, in a sealed tube to 140° for some hours. The liquid portion is filtered from the potassium iodide, the alcohol evaporated off, and the oily residue boiled for some time with dilute soda-ley. After cooling, the liquid is acidulated with sulphuric acid, by which means a flocculent deposit of the new acid is produced. This is shaken up with ether, and the insoluble residue repeatedly crystallised from water. It is obtained in glistening, white needles, having the composition $C_6H_3\begin{cases}OCH_3\\OCH_3\\COOH.\end{cases}$ It melts at 170°—171°, and does not show the characteristic iron reaction of protocatechuic acid. By distillation with lime, it gives rise to an oil, boiling between 210° and 215°, and having the composition of dimethyl-pyrocatechin:

$$C_6H_4\begin{cases}OCH_3\\OCH_3.\end{cases}$$

"The acid is converted by bromine into *bromodimethyl-protocatechuic acid*, $C_6H_2Br.(OCH_3)_2.COOH$, which crystallises from water in needles.

"*Diethyl-protocatechuic acid*, $C_6H_3\begin{cases}OC_2H_5\\OC_2H_5\\COOH\end{cases}$ is prepared in a similar manner to the dimethyl-acid. It melts at 149°, and gives no reaction with iron perchloride. By dry distillation it yields an oil, probably consisting of

diethyl-pyrocatechin. With bromine it forms a crystalline product, exhibiting the composition of a mixture of mono- and di-bromodiethyl-pyrocatechuic acid.

III.

Salts of Ethylene-protocatechuic Acid.

Ethylene-protocatechuate of Calcium $(C_9H_7O_4)_2\,Ca + 2H_2O$.

Ethylene-protocatechuic acid was dissolved in boiling water, and carbonate of calcuim added until the acid was saturated. The excess of carbonate of lime was filtered off and the solution set aside to crystallise. On allowing the solution to crystallise slowly, beautiful large monoclinic crystals were formed, about a centimetre in length.

The calcium salt is difficultly soluble in cold water and not very easily soluble even in boiling water. Like piperonylate of lime it gives with chloride of iron a yellow precipitate.

0·2303 gramm substance, lost between 150°—200°: 0·0194 gramm water, and gave 0·0706 gramm sulphate of calcium = 0·02076 gramm calcium.

H_2O = 8·42 per cent. Ca = 9·01 per cent.

		Calculated.		Found.
$(C_9H_7O_4)_2$	358	82·49	——	——
Ca	40	9·21	——	9·01
$2HO_2$	36	8·30	——	8·42
	434	100·00		

Ethylene-protocatechuate of Barium $(C_9H_7O_4)_2$ Ba$+2H_2O$.

The barium salt of ethylene-protocatechuic acid was prepared by adding carbonate of barium to a solution of the acid in boiling water. When the solution shewed an alkaline reaction with litmus paper, the excess of carbonate of barium was filtered off, and the filtrate set aside to crystallise.

The crystals of ethylene-protocatechuate of barium are very beautiful, hard, compact crystals. They are almost absolutely insoluble in cold water, and dissolve with difficulty in boiling water. Like the lime salt of ethylene-protocatechuic acid, and the lime and barium salts of piperonylic acid, it gives with chloride of iron a yellow precipitate.

0·2224 gramm substance, lost at 150°: 0·0151 gramm water, and gave 0·0976 gramm sulphate of baryta = 0·05738 gramm barium.

H_2O = 6·79 per cent. Ba = 25·80 per cent.

	Calculated.		Found.
$(C_9H_7O_4)_2$	358 — 67·42	—	—
Ba	137 — 25·80	—	25·80
$2H_2O$	36 — 6·78	—	6·79
	531 100·00		

Ethylene-protocatechuate of Soda $C_9H_7O_4$ Na$+(H_2O$?)

Ethylene-protocatechuate of soda was prepared by cautiously adding a solution of carbonate of soda to a

solution of ethylene-protocatechuate of lime, until a precipitate ceased to fall. The carbonate of lime was then filtered off, and the filtrate evaporated and set aside to crystallise.

The soda salt of ethylene-protocatechuic acid is so very easily soluble in water and alcohol, that even although it be allowed to evaporate spontaneously it does not crystallise out. Being so very easily soluble nothing could be done with it, so it was acidified with hydrochloric acid, and the ethylene-protocatechuic acid extracted from the solution by means of ether.

IV.

Ether of Ethylene-protocatechuic Acid.

About 2 gramms of ethylene-protocatechuic acid were dissolved in absolute alcohol, and dry hydrochloric acid gas passed through the solution for some time after it had apparently ceased to absorb the gas. The flask containing the solution of the ether of ethylene-protocatechuic acid was connected with a reversed cooler, and the contents boiled on a water bath until the hydrochloric acid gas ceased to come over. The alcohol was then distilled off, and the remainder, which was half solid, was shaken with carbonate of soda to extract any undecomposed ethylene-protocatechuic acid. After shaking for some time, the

ether, which before this was liquid, changed to a slightly discoloured amorphous powder. It was filtered off, well washed with cold water, pressed between white bibulous paper, dissolved in alcohol, boiled with animal charcoal, filtered, evaporated, and set aside to crystallise; but it did not crystallise even when reduced to a very small bulk.

The ether of ethylene-protocatechuic acid is very easily soluble in alcohol, from which solvent it separates at the ordinary temperatures as a liquid. On cooling in a mixture of salt and ice the ether solidifies.

As these investigations were carried on in the middle of winter it was found convenient to work in a cold room, the temperature of which was equal to—3 or 4°.

The solid ether was filtered off, well washed with cold water, and put over sulphuric acid in the cold room.

As stated before, the ether of ethylene-protocatechuic acid is a slightly coloured amorphous powder, very easily soluble in cold and hot alcohol. It melts instantaneously at 27—28°.

The substance was dried by allowing it to stand over sulphuric acid for some days. The results of the analyses were as follow:

I. 0·0975 gramm substance gave 0·0543 gramm H_2O = 0·006033 H, and 0·2280 gramm CO_2 = 0·062181 C.
C = 63·77 per cent. H = 6·18 per cent.

II. 0·2074 gramm substance gave 0·1073 gramm H_2O = 0·011922 H, and 0·4797 gramm CO_2 = 0·13083 C.
C = 63·08 per cent. H = 5·75 per cent.

These results agree with the formula

$$C_{11}H_{12}O_4 \quad \text{or} \quad C_6H_3\begin{cases} O \\ O \\ CO.OC_2H_5 \end{cases}\!\!>C_2H_4$$

	Calculated.		Found.	
			I.	II.
C_{11}	132	63·46	63·77	63·08
H_{12}	12	5·77	6·18	5·75
O_4	64	30·77	—	—
	208	100·00		

V.

Action of Dilute Hydrochloric Acid on Ethylene-protocatechuic Acid.

Some pure ethylene-protocatechuic acid was put into a strong glass tube, weak hydrochloric acid—1 of concentrated hydrochloric acid to 10 of water—added and the tube hermetically sealed. It was then heated to 220° for several hours but without any sign of decomposition. The temperature therefore was raised until the thermometer indicated 260° and kept at that point for three or four hours. On taking the tube from the air bath, it was plainly evident that a decomposition had taken place, for, lying at the bottom of the tube was a black shining substance, while the solution above was clear.

The gas generated was tested. On breaking open the end of the tube there was little pressure, but on heating the contents a gas was given off. On leading the gas, first, into an ammoniacal solution of cuprous chloride, no precipitate was obtained, which showed the absence of acetylene gas, but on testing with lime water a white precipitate proved the presence of carbonic acid gas. The contents of the tube were filtered from the finely divided carbon, and the filtrate evaporated to dryness on a water bath to get rid of the hydrochloric acid. The residue was boiled with toluene to extract any pyrocatechin which might have been formed by the high temperature. All dissolved except a little of a black substance, which was thrown away, as there was not enough to work upon. On evaporating the toluene solution to dryness, a white powder was obtained which gave the characteristic reactions of pyrocatechin, namely, a dark green colour with chloride of iron, which, on the addition of carbonate of soda changed to violet.

In this research so little substance was obtained by each experiment that it was deemed advisable to leave it over and investigate the action of phosphorous pentachloride on ethylene-protocatechuic acid.

As the result of this investigation, it appeared, that on heating ethylene-protocatechuic acid with dilute hydrochloric acid, the only products of decomposition were carbon, pyrocatechin, carbonic acid, and probably hydrogen.

If we compare the action of dilute hydrochloric acid and of water on piperonylic acid with that of dilute hydrochloric acid on ethylene-protocatechuic acid, we notice a similarity. In the case of piperonylic acid and dilute

hydrochloric acid, finely divided carbon and protocatechuic acid were obtained, while in that of piperonylic acid and water, finely divided carbon, pyocatechin, and probably carbonic acid.

In the treatment with dilute hydrochloric acid the temperature was only 170°, a heat incapable of decomposing protocatechuic acid to pyrocatechin, while in that with water the heat was raised to 210°, a temperature sufficient to produce pyrocatechin. So in the treatment of ethylene-protocatechuic acid with dilute hydrochloric acid, it was necessary to heat the contents of the tube to 260° before any change took place.

If the temperature had been raised higher in the action of dilute hydrochloric acid on piperonylic acid, pyrocatechin would almost certainly have resulted.

The action of dilute hydrochloric acid is therefore very simple, and may be expressed in the following equations:

$$(1)\quad C_6H_3\begin{cases} O{-}CH_2 \\ \quad | \\ O{-}CH_2 \\ COOH \end{cases} = C_6H_3\begin{cases} OH \\ OH \\ COOH \end{cases} + 2C + 2H$$

$$(2)\quad C_6H_3\begin{cases} OH \\ OH \\ COOH \end{cases} = C_6H_4\begin{cases} OH \\ OH \end{cases} + CO_2.$$

There is one thing, however, which seems to argue that there is something amiss. Seeing that there was so little pressure on opening the tube, what became of the two atoms of hydrogen mentioned at the end of the first equation?

VI.

On the Decomposition of Ethylene-protocatechuic Acid by Phosphorous Pentachloride.

1. Experiment with one molecule of Ethylene-protocatechuic acid to three molecules of Phosphorous Pentachloride.

a. In an open vessel.

Three molecules of phosphorous pentachloride and one molecule of ethylene-protocatechuic acid—the same proportions as those used in the experiment with piperonylic acid by Fittig and Remsen—were introduced into a dry retort having a thermometer in the neck. On heating gently, the whole became liquid, and hydrochloric acid gas was copiously evolved. When the mercury in the thermometer indicated 99°, the contents of the retort began to boil, and a liquid distilled over which was caught in a dry receiver placed for the purpose of collecting it that it might afterwards be tested to decide whether chloroxyde, or terchloride of phosphorous, or both had been formed. After heating for some time with a very small flame and nothing more coming over, the lamp was withdrawn. The liquid did not solidify even when allowed to stand for some time in the cold. On pouring it into a beaker containing cold water, for the purpose of decomposing any remains of the chloride of phosphorous that might adhere to it, it sank to the bottom and remained quiet for some time.

Soon, however, action commenced, and bubbles of gas were slowly disengaged. When no more gas was given off, the thick, flesh-coloured, oily substance was washed several times by decantation with cold water, then transferred to a flask with a little water and boiled until all dissolved. It was filtered and set aside to crystallise.

After crystallising several times, a very easily soluble substance was obtained. It gave the characteristic reactions of protocatechuic acid, namely, a dark green colour with chloride of iron, which turned to red on the addition of a drop of carbonate of soda. The crystals gave the fusing point 194°, but the lowness may be accounted for by a slight impurity. Pure protocatechuic acid melts at 199°. A large quantity of ethylene-protocatechuic acid was also recovered, which had escaped decomposition by phosphorous pentachloride.

It appears from these results, that on treating ethylene-protocatechuic acid with phosphorous pentachloride, an oil is obtained which is easily decomposed to protocatechuic acid by treating with boiling water.

As these experiments were not so satisfactory as could be desired, it was decided to allow the ethylene-protocatechuic acid and phosphorous pentachloride to act together in a sealed tube for a longer time, at a somewhat higher temperature.

b. In a sealed tube.

Ethylene-protocatechuic acid and phosphorous pentachloride, in the proportions of one molecule of the acid to three molecules of the chloride, were put into a strong glass tube

which was sealed at one end. The other end was fused together until there was only a small aperture left, so that it could be easily sealed when it was desired to do so. The tube was now placed in a water bath kept at 100°. At about 96° gases began to come off, violent action took place, and the substances became liquid, except a little phosphorous pentachloride. (On taking the tube out of the bath and allowing it to cool, the liquid became solid again.) When the action had ceased the tube was hermetically sealed, again placed in the water bath and heated to 100° for three hours. As the phosphorous pentachloride would not all dissolve, the tube was taken out, enclosed in a strong iron tube, and heated in the air bath for seven hours at 130°.

When the tube was taken out of the air bath, all the phosphorous pentachloride had disappeared, and a watery clear liquid filled its place. The tube was opened, not by the usual method of heating the end of the tube and allowing the gas to burst through, but by filing the end and chipping it off, so as to leave a very small opening.

There is great danger in the first method, as there is always a very strong rush of gas, causing violent ebullition of the liquid, and if the opening be too large the liquid mounts to the hot part, where, being suddenly converted into vapour, it causes the tube to fly to pieces. But in the other case, if the hole should be chipped too large, the tube has only to be suddenly inverted, when the gas from the inside will inject it into a dry beaker placed there for the purpose.

When the rush of gas had ceased, the tube was broken near the middle, the liquid poured into a beaker containing water, and the tube washed out several times with cold water. On pouring the liquid into the water, it sank to

the bottom and changed to a white fleshy oil, remaining quiet for some time. Soon, however, action began to take place, bubbles of gas were given off, and the action continued for about half-an-hour. The oily substance was allowed to stand under water in the beaker for twenty-four hours, to see if it would become hard, but at the end of that time it still retained its semi-solid appearance.

Taking into account its disagreeable properties, it was decided to leave the analysis over, and to investigate the action of hot water on this semi-solid substance. It is probably dichlorethylene-protocatechuic-chloride.

Action of Hot Water on Dichlorethylene-protocatechuic Chloride.

a. In an open vessel.

Some of the substance was transferred to a flask and a little water added. The flask was connected with a distilling apparatus, to condense any volatile substance which might be formed. The water in the flask was heated slowly to boiling. On heating, the semi-solid substance changed to a light amber coloured oil, then an action, like effervescence, began, and although the lamp was withdrawn the action continued until the oil disappeared. What is remarkable, is, that no gas apparently was given off.

The contents of the flask were evaporated to a small bulk, filtered, and set aside to crystallise. Small dark

crystals separated out and were filtered off. They were then pressed between bibulous paper to remove as much as possible of the mother liquor clinging to them, again dissolved in boiling water, and allowed to crystallise. On dissolving the crystals in water, and testing with chloride of iron and carbonate of soda, reactions were given which resembled those of protocatechuic acid.

The dry crystals gave the melting point 196°, but the lowness may be accounted for by a slight impurity. Pure protocatechuic acid melts at 199°.

b. In a sealed tube.

It was supposed, that if instead of boiling the substance in an open vessel with water, it were heated with water in a closed tube, the action would be much more rapid.

What remained of the semi-solid substance was enclosed with water in a strong glass tube, and heated to 100° for three hours in a water bath. The substance did not dissolve, but on cooling became very hard and brittle. On opening the tube, not the slightest pressure of gas was perceptible. The solution was filtered from the hard white substance, and the filter and substance well washed with cold water.

The filtrate was shaken with ether, the etherial solution drawn off by means of a pipette and run into a dry flask. On distilling off the ether, dissolving the residue in water, evaporating, and allowing to crystallise, a substance was obtained which was easily soluble in cold and hot water. It gave the same reactions as protocatechuic acid, and

possessed the fusing point 198°. It gave, on analysis, numbers which shewed it to be protocatechuic acid.

The insoluble substance, mentioned above, was transferred to a mortar and pulverised. A little water, and a few drops of carbonate of soda were added, and all stirred by means of the pestle. Everything dissolved. The solution was filtered, acidified by hydrochloric acid, the white precipitate which formed filtered off, washed well with cold water, and put over sulphuric acid.

This substance, which is perfectly insoluble in water, whither cold or hot, decomposes when boiled with water in an open vessel. It is easily soluble in alchol and ether, from which solutions it is readily precipitated again as an oil on the addition of water. It fuses at 118°—120°.

The substance was dried thoroughly by means of standing over sulphuric acid, and then analysed with the following results:

I. Combustion.

0·1898 gramm substance gave 0·2943 gramm CO_2 = 0·08026 C, and 0·0428 gramm H_2O = 0·00475 H.

C = 42·28 per cent. H = 2·50 per cent.

II. Chlorine Estimation.

0·1850 gramm substance heated with water to 130° for six hours in a sealed tube, strongly acidified with nitric acid, and treated with a solution of nitrate of silver, gave 0·2367 gramm Ag Cl = 0·058556 Cl.

Cl = 31·65 per cent.

	Calculated.		Found.		Calculated.	
C_9 —	108	43·37	42·28	C_9 —	108	38·10
H_6 —	6	2·41	2·50	H_5 —	5	1·76
Cl_2 —	71	28·51	31·61	Cl_3 —	106·5	37·56
O_4 —	64	25·70	——	O_4 —	64	22.57
	249	100·00			283·5	100·00

This analysis proves pretty positively that the compound formed has the empirical formula $C_9H_6Cl_2O_4$, but at the same time it appears that there is a little $C_9H_5Cl_3O_4$ present.

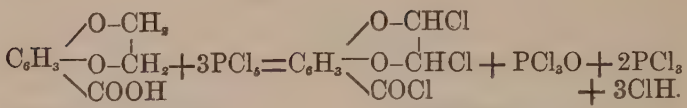
Owing to the insolubility of this substance in water, and its too ready solution in acohol and ether, it could not be purified. I had therefore to take it as it was, and accept the results of its analysis.

CONCLUDING REMARKS.

From these results it appears very clearly that when three molecules of phosphorous pentachloride are allowed to act on one molecule of ethylene-protocatechuic acid, reactions ensue, and substances are obtained which may be expressed by the following equations:

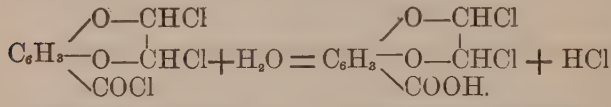
The ethylene-protocatechuic acid allows the chlorine atoms to replace first the hydroxyle of the carboxyle group, and then two hydrogens of the ethylene group forming

a semi-solid substance, dichlorethylene-protocatechuic chloride:



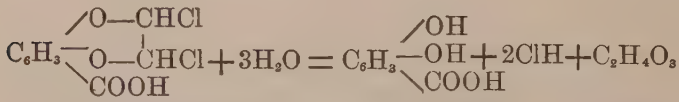
Ethylene-protocatechuic acid. Dichlorethylene-protocatechuic chloride.

Which substance, when treated with water, again recovers its hydroxyle, and changes to a white, fleshy, semi-solid substance, dichlorethylene-protocatechuic acid:



Dichlorethylene-protocatechuic chloride. Dichlorethylene-protocatechuic acid.

Again, on heating dichlorethylene-protocatechuic acid with water to about 130°, protocatechuic acid and probably glycollic acid are obtained:



Dichlorethylene-protocatechuic acid. Protocatechuic acid. Glycollic acid.

2. Experiment with Excess of Phosphorous Pentachloride.

The ethylene-protocatechuic acid was introduced into a strong glass tube and a large excess of phosphorous pentachloride added. The tube was fused together at the other end as in the former experiment, until only a very small aperture remained for the escape of the gases. The

tube was heated in the water bath until the violent action which ensued had ceased, and until the gases ceased to come over. There was still a large excess of phosphorous pentachloride. The tube was hermetically sealed, placed in an iron tube, and heated in the air bath to 130°—150° for about ninety hours. There was still a little undecomposed chloride. It had not, to all appearance, been taken up after heating for half the time, so that the decomposition could have been performed in a much shorter time. The solution had a slightly yellowish tinge. On opening the tube, there was as usual, a very strong rush of gas. The contents of the tube were poured into a beaker containing water, the undecomposed phosphorous pentachloride shaken out, and the tube rinsed out several times with cold water. After a little a few bubbles of gas were given off from the white, fleshy, semi-solid substance lying under the water, the action continuing for some time as in the former experiment. The beaker and its contents were allowed to stand over for twenty-four hours.

On pouring the contents of the tube into the water, the liquid changed to an almost white, semi-solid substance, but by the next day this substance had become hard and brittle. In the experiments with one molecule of the acid to three molecules of the chloride, the substance had not become hard except when exposed to intense cold.

The substance was treated with cold carbonate of soda,—in which it is perfectly insoluble,—to dissolve out any ethylene-protocatechuic acid which might have escaped decomposition. The insoluble was filtered off, very well washed with cold distilled water, and put over sulphuric acid.

This substance is perfectly insoluble in cold water, but decomposes with hot water. It is very easily soluble in ether and alcohol, from which solutions it is again precipitated as an oily liquid on the addition of water.

It is perfectly insoluble in carbonate of soda. On heating to about 60° it becomes dark, and melts between 70° and 80°, the exact point being indiscernible on account of the darkening.

After drying over sulphuric acid it was analysed with the following results:

COMBUSTIONS.

I. 0·2261 gramm substance gave 0·2333 gramm CO_2 = 0·06518 C and 0·0234 gramm H_2O = 0·003288 H.

C = 28·14 per cent. H = ·15 per cent.

II. 0·2294 gramm substance gave 0·2390 gramm CO_2 = 0·06518 C and 0·0234 gramm H_2O = 1·13 H.

C = 28·40 per cent. H = ·13 per cent.

CHLORINE ESTIMATION.

III. 0·3151 gramm substance heated with water to 140° —150° for nine hours in a sealed tube, strongly acidified with nitric acid, and treated with a solution of nitrate of silver, gave 0·7486 gramm AgCl = 0·18518 Cl.

Cl = 58·77 per cent.

Calculated.			Found.				Calculated.	
			I.	II.	III.			
C_9	108	27·90	28·40	28·14	—	C_9	108	25·62
H_2	2	·52	·13	·15	—	H	1	·23
Cl_6	213	55·04	—	—	58·77	Cl_7	248·5	58·96
O_4	64	16·54	—	—	—	O_4	64	15·19
	387	100·00					421·5	100·00

From these analyses it appears that there is a mixture of the two substances $C_9H_2Cl_6O_4$ and $C_9HCl_7O_4$. Taking into account that it was impossible to purify them, the analyses agree very well with one another.

Action of Hot Water on $C_9H_3Cl_7O_2$.

a. In an open vessel.

Some of the substance was boiled with water in a flask for about six hours, but at the end of that time very little of it had decomposed. No effervescence took place, as in the former experiment, but the solution boiled very irregularly, so that there was great danger of it boiling over. When heated *under* water the substance melted at a point a little above the ordinary temperature of the water, and about boiling water heat it changed to a thin oil.

The liquid was filtered from the undecomposed oily substance, acidified with hydrochloric acid, shaken with ether, the etherial solution drawn off by means of a pipette and emptied into a dry flask. After distilling off the ether the remainder was dissolved in water, and allowed to crystallise. It gave slightly discoloured crystals, which were filtered off, dissolved in water, and again allowed to crystallise. The crystals which were thus obtained, after drying, gave the fusing point 198°. With chloride of iron they gave a green colour, which on the addition of carbonate of soda changed to red. In consideration of these facts, its identity as protocatechuic acid cannot well be doubted.

b. In a sealed tube.

The compound which results from the treatment of ethylene-protocatechuic acid with excess of phosphorous pentachloride, is, as we have seen, with great difficulty decomposed by boiling water in an open vessel. It is also with difficulty decomposed by hot water in a hermetically sealed tube. A small quantity of the substance was put into a tube with some water. The tube was hermetically sealed, and heated in a water bath—which was kept boiling—for twenty hours.

While being heated, the solid substance became soft and semi-liquid. It also decreased in bulk, and on allowing to cool, it became hard and brittle again. On opening the tube, no gas made itself known.

The solution was filtered from the solid substance, and by the ordinary tests, proved to contain protocatechuic acid and hydrochloric acid.

The hard brittle substance was well washed, transferred to a mortar, a few drops of carbonate of soda and a little water added, and the whole stirred about until everything dissolved, except a little insoluble. The solution was filtered from the insoluble in carbonate of soda, acidified with hydrochloric acid, the precipitate filtered off, well washed, and put over sulphuric acid to dry.

The substance was dried thoroughly by means of standing over sulphuric acid, and then the chlorine was estimated; with the following results:

I. Chlorine Estimation.

0·1002 gramm substance heated with water to 130°—150° for eighteen hours in a sealed tube, strongly acidified with nitric acid, and treated with a solution of nitrate of silver, gave 0·1862 gramm AgCl = 0·046063 Cl.

Cl = 45·97 per cent.

		Calculated.				Found.
C_9	——	108	——	33·96	——	——
H_4	——	4	——	1·26	——	——
O_4	——	64	——	20·13	——	——
Cl_4	——	142	——	44·65	——	45·97
		318		100·00		

The chlorine estimation came so close to the theoretical amount that an organic analysis was considered superfluous.

This substance is insoluble in cold water, but decomposed when heated with water to a high temperature in a sealed tube. It is very easily soluble in cold *dilute* carbonate of soda. It is also easily soluble in alcohol and ether, at all temperatures, in almost any proportions; and may again be precipitated from the alcoholic solution by adding water.

To complete the investigation of the action of phosphorous pentachloride on ethylene-protocatechuic acid, it was desirable to discover what substances were formed when any of the chlorine compounds were heated with water at a high temperature. For this purpose $C_9H_4Cl_4O_4$ was placed in a tube with some water, and the tube hermetically sealed, and heated in the air bath to 130°. It was necessary to heat for eighteen hours before the substance disappeared. On opening the tube, not the slightest

pressure of gas was perceptible. A portion of the slightly discoloured liquid was tested with nitrate of silver, when a large precipitate shewed the presence of hydrochloric acid in abundance.

The remainder of the solution was agitated with ether, the etherial solution drawn off by means of a pipette and ejected into a dry flask. The ether was distilled off, and the residue dissolved in hot water, in which it was easily soluble. The slightly discoloured solution was treated with animal charcoal, filtered, and allowed to crystallise. The crystals which separated were filtered off, again dissolved in boiling water, and set aside to crystallise. One thing in particular was noticable, that when the crystals were allowed to stand in the solution, the needle shaped crystals changed to prisms, which is a characteristic property of protocatechuic acid. The crystals which then separated were perfectly pure, possessing the fusing point 199°.

On testing the solution with chloride of iron, a dark green colour was obtained, which on the addition of carbonate of soda changed to red. To settle the identity of the substance beyond dispute the analysis was performed:

I. Estimation of Water of Crystallisation.

0·1507 gramm substance lost, on being heated to 130°, 0·0166 gramm = water.

$H_2O = 11·01$ per cent.

II. Combustion.

0·1341 gramm substance dried at 130° gave 0·2696 gramm $CO_2 = 0·073527$ C, and 0·0483 gramm $H_2O = 0·005366$ H.

C = 54·81 per cent. H = 4·00 per cent.

	Calculated.		Found.
C_7	84	54·54	54·81
H_6	6	3·89	4·00
O_4	64	41·57	——
	154	100·00	

	Calculated		Found.
$C_7H_6O_4$	154	89·54	——
H_2O	18	10·46	11·01
	172	100·00	

It appears from this experiment that at least two substances are formed, namely, hydrochloric acid and protocatechuic acid.

Experiments to prove the Identity of Carbohydroquinonic and Protocatechuic Acids.

While engaged investigating ethylene-protocatechuic acid, it occurred to me that it would be exceedingly important to allow some of the same reagents to act on carbohydroquinonic acid.

In preparing carbohydroquinonic acid I followed the method proposed by Hesse.* Bromine is added to a watery solution of quinic acid, by portions of ten drops each, till a portion of it remains undissolved, even after the liquid has been frequently agitated and allowed to stand for twelve hours. The solution which is then decanted from the undissolved bromine—evaporated on the water bath, and shaken up with ether—yields to this liquid carbohydroquinonic acid, which, after the ether has been distilled off, remains as a brown crystalline residue. It is purified by recrystallisation from water with help of animal charcoal.

Carbohydroquinonic acid crystallises from its aqueous solution with one atom of water ($C_7H_6O_4.H_2O$) in furcate groups of needles, also in rhombic laminae or granular crystals. It dissolves very easily in boiling water and in alcohol. The anhydrous acid melts at 199°.

* Annalen der Chemie u. Pharm. cxii, 52.

One peculiarity worthy of mention I noticed while preparing this acid. If, after shaking with bromine and allowing to rest for twelve hours, the solution be evaporated on the water bath, with continual stirring until the bromine entirely disappears, and, after allowing to cool, the solution be shaken with ether, on distilling off the ether scarcely anything remains behind. As so little was obtained, the solution was evaporated on a water bath to a very small bulk, and shaken with ether. On distilling off the ether a large quantity of carbohydroquinonic acid remained behind. It seems from this phenomenon that hydrobromic acid has played a reducing part in the formation of carbohydroquinonic acid.

On allowing crystals of carbohydroquinonic acid to remain in the solution from which they crystallise, they change from the needle shaped crystals in which they first appear to small cubes. This property of changing the crystalline form has been mentioned by several chemists, who have investigated protocatechuic acid as a peculiar characteristic of that substance.

I.

Ether of Protocatechuic Acid.

This substance was prepared by dissolving protocatechuic acid in ninety per cent. alcohol, and passing dry hydrochloric acid gas through the solution for some time after it had apparently ceased to absorb the gas. The flask was

now connected with a reversed cooler, and the solution boiled in a water bath until the excess of hydrochloric acid gas was driven off. The cooler was then changed to the well known position for distilling, and the alcohol distilled off. After distilling off the alcohol, what remained in the flask was evaporated to dryness. The dry residue was treated with a solution of carbonate of soda—to dissolve out any protocatechuic acid which might have escaped decomposition—the solution filtered, washed well with cold water, dissolved in hot water, and set aside to crystallise.

The ether of protocatechuic acid melts in boiling water before dissolving; it is easily soluble in alcohol, and especially in ether. It is crystalline and melts at 133° —134°. Dissolved in alcohol and allowed to crystallise slowly over sulphuric acid, it gives white warty crystals.

The ether was dried at 100° in an air bath and then analysed:

Combustion.

0·2103 gramm substance, dried at 100° gave 0·4550 gramm $CO_2 = 0·1241$ C and 0·1105 gramm $H_2O = 0·012277$ H.

C = 59·01 per cent. H = 5·83 per cent.

		Calculated.				Found.
C_9	——	108	——	59·34	——	59·01
H_{10}	——	10	——	5·49	——	5·83
O_4	——	64	——	35·17	——	——
		182		100·00		

This substance has the same crystalline appearance, the same melting point, and gives the same numbers by analysis as the ether of carbohydroquinonic acid mentioned by Hesse.*

* Annalen der Chemie u. Pharm. cxiv. 292.

II.

Ethylene-carbohydroquinonic Acid.

Carbohydroquinonic acid, caustic potash, and ethylene-bromide, in the same proportions as for the preparation of ethylene-protocatechuic acid, were put into a strong glass tube with a few drops of water. The tube was then hermetically sealed and heated in warm water. The contents darkened at once and soon became liquid. The tube and its contents were heated for five or six hours in the water bath which was kept boiling. On opening the tube there was a strong rush of gas. The contents were dissolved out by means of water, the ethylene-bromide distilled off, and the remaining solution acidified by means of hydrochloric acid.

The solution was filtered, while hot, from the black substance which fell out, shaken with ether, the ether distilled off, and the residue dissolved in water and purified by several crystallisations, assisted by animal charcoal.

Ethylene-carbohydroquinonic acid gives crystals similar in every respect to those obtained from ethylene-protocatechuic acid. It is difficultly soluble in cold water, but in boiling water it dissolves very readily. In alcohol it is soluble in every proportion. It melts at 133·5.

As ethylene-carbohydroquinonic acid agreed so very closely with ethylene-protocatechuic acid, it was deemed unnecessary to analyse it.

III.

Ethylene-carbohydroquinonate of Calcium.

The calcium salt forms large colourless crystals, closely resembling ethylene-protocatechuate of calcium. They were difficultly soluble in cold water, and not much more readily in boiling water. It is prepared by neutralising a watery solution of ethylene-carbohydroquinonic acid with carbonate of calcium.

On analysis it gave numbers as follow:

I. Lime Estimation.

0·1846 gramm substance lost between 150—200°
0·0159 gramm H_2O and gave 0·0579 gramm
sulphate of calcium = 0·01703 gramm Ca.
H_2O = 8·61 per cent. Ca = 9.22 per cent.

	Calculated.		Found.
$(C_9H_7O_4)_2$	358	82·49	—
Ca	40	9·21	9·22
$2H_2O$	36	8·30	8·61
	434	100·00	

Comparison of Ethylene-protocatechuic Acid and Ethylene-carbohydroquinonic Acid.

If we place the two acids side by side, we will be better able to compare the results of this investigation with that of other investigations.

The first, and one of the most important similarities, was the changing of the form of the crystals of carbohydroquinonic acid and protocatechuic acid from needles to cubes on standing in the solution, from which they crystallised.

The ether of protocatechuic acid is very like the ether of carbohydroquinonic acid described by Hesse*. It fuses at 134°. On heating under water it melts before dissolving. It is very easily soluble in alcohol and ordinary ether. An analysis gave numbers agreeing exactly with the formula for the ether of carbohydroquinonic acid.

Both ethylene-carbohydroquinonic and ethylene-protocatechuic acid when heated with caustic potash and ethylene-bromide in a sealed tube in a water bath, darkened at once, and on continuing the heating became liquid. When the tubes were opened, the contents dissolved out with water, and acidified with hydrochloric acid, a black substance fell in each case which behaved alike on being treated with water, ether, and ammonia.

* Annalen der Chemie u. Pharm cxiv. 292.

The crystals of ethylene-carbohydroquinonic acid and ethylene-protocatechuic acid were alike in every respect to one another. They were difficultly soluble in cold water, but dissolved much more readily in hot water. The dried crystals of each acid melted instantaneously at 133·5.

Ethylene-carbohydroquinonate of lime crystallises in the same form as ethylene-protocatechuate of lime. The crystals of the two salts were alike difficultly soluble in cold water, and even in hot water they dissolved with difficulty.

Taking these facts into consideration, along with those mentioned by the Chemists* who have been engaged on the investigations of the same substance, it is next to impossible that the two substances can be different.

* Hesse Annalen der Chemie u. Pharm cxii. 527; cxiv. 292; cxxii. 22.
Lautemann do. do. cxx. 315.

Paisley, 18th July 1872.